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(54) Title: LASER ABSORPTION WAVE DEPOSITION PROCESS			
(57) Abstract			
<p>There is disclosed herein a pulsed laser method for forming film coatings from a gas, such as H₂ (22) and a hydrocarbon (24). The gas mixture input by line (20) and nozzle (18) is ignited by laser (12) to form flame (26) and then irradiated by a laser pulse (14) at an energy level above the threshold breakdown level of the gas to create a seed plasma in the gas at (28). Subsequent energy from the laser pulse is absorbed to form a plasma excitation called a laser absorption wave (30). The laser absorption wave is a wall of energy which detaches from the seed plasma and propagates through the gas (30a, b). The film growth precursor fragments of the gas are generated by the laser absorption wave and deposited onto a substrate (32 or 34) welding to its surface to form a coating. The substrate surface may be partially liquefied or evaporated forming precursor fragments of the substrate that mix with the precursor fragments of the gas that weld to the substrate forming a coating.</p>			

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LASER ABSORPTION WAVE DEPOSITION PROCESS**BACKGROUND OF THE INVENTION****FIELD OF THE INVENTION**

Diamond coatings are in great demand as protective coatings for number of materials, as hardness coatings on various machine tools, and as electronic materials, owing largely to the qualities of high thermal conductivity, electron mobility, and radiance resistance. Furthermore, diamond also finds application as a cold cathode material due to its high, negative electron affinity. Such cold cathode applications will make possible flat panel displays and is identified as an excellent drug delivery system due to its chemical inertness, lack of biodegradation, and the ability of various organic molecules to reversibly bind to its surface.

Because of the great demand, techniques have been developed to apply diamond coatings to a wide variety of materials. Common to all the production techniques is the formation of a plasma as a source of atomic hydrogen and diamond precursors. Conventional chemical vapor deposition methods require substrate heating to temperatures between 800 to 1000° C. as well as low gas pressures to tens of torr to ensure the diffusion of material from the plasma to a solid state target substrate. In the case where diamond growth takes place at atmospheric pressure, using the flame techniques pioneered by Hirose, substrates tend to over heat beyond the desirable substrate temperatures, thus requiring the active cooling of the target substrate. Alternately, pressures of tens of thousands of atmospheres and thousands of degrees are used to create high pressure, high temperature diamond within molten acetylide salts.

In U. S. Patent 4,981,717 assigned to the assignee of the instant application, there was disclosed a method of depositing diamond coatings wherein the method generated a plasma by absorption of the laser radiation into a precursor gas or a gas mixture at atmospheric pressure. The laser pulse is absorbed by the initiator gas which is mixed in with precursor gases such as hydrocarbon, for example, methane, ethane propane, ethylene, acetylene. The initiator is preferably a compound which is strongly absorbing at the output wavelength of the laser pulse

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1 which is strongly absorbing at the output wavelength of the laser pulse
2 used. The shock wave associated with the sudden absorption of laser
3 radiation was utilized in transporting ions radicals, and molecular
4 fragments onto a suitably positioned substrate. The diamond like coatings
5 formed were of a carbonaceous species having characteristics of hardness
6 and chemical structure similar to diamond.

8 SUMMARY OF THE INVENTION

10 There is provided by this invention a general pulsed laser method
11 for forming film coatings from a gas phase. A seed plasma is created in the
12 gas via an intense, focused laser pulse forming an initiating material.
13 Subsequent energy from the laser pulse is absorbed to form a plasma
14 excitation called a laser absorption wave. The laser absorption wave is a
15 wall of energy which detaches from the seed plasma and propagates
16 through the gas. The film growth precursors are generated by the laser
17 absorption wave onto a substrate welding to its surface to form a coating.
18 The substrate surface is partially liquefied or evaporated allowing the
19 coating materials to weld to the substrate.

21 BRIEF DESCRIPTION OF THE DRAWINGS

23 FIGURE 1 is a schematical diagram of apparatus for performing the
24 laser deposition process incorporating the principles of the inventions
25 herein;

26 FIGURE 1A is alternate embodiment of the schematical diagram
27 shown in FIGURE 1 having a substrate reflective of the laser beam;

28 FIGURE 2 is a schematical diagram of apparatus for the laser
29 deposition process having a substrate transmissive to the laser beam;

30 FIGURE 3 is a schematical embodiment of the laser deposition process
31 illustrating ablation of the substrate;

32 FIGURE 3A is an alternate embodiment of the ablation process shown
33 in FIGURE 3; and

34 FIGURE 4 is a schematical embodiment of the laser deposition process
35 illustrating laser heating of the substrate.

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1 BRIEF DESCRIPTION OF THE PREFERRED EMBODIMENT

2
3 There is shown in FIGURE 1 the laser absorption wave apparatus 10
4 that is generally comprised of a laser 12 that emits a laser pulse 14 that is
5 focused by a lens 16 into a gas stream emitting from the nozzle 18. The
6 gases emitted from the nozzle 18 are combined in the gas line 20 that is
7 supplied by gases from a hydrogen input 22 and a hydrocarbon gas input
8 24. The hydrocarbon gas maybe any gas containing the fragment having
9 the chemical formula C_xH_y . The irradiation of the gas by the laser ignites
10 a flame 26 and above threshold levels for avalanche breakdown creates an
11 electron seed plasma at 28. The flame 26 also serves to heat the
12 substrate. It should be noted here that in some applications the process
13 herein described is performed in a closed chamber filled with an inert gas
14 to eliminate the flame 26. Further excitation by the laser creates a laser
15 absorption wave generally shown at 30. The pulse width of the laser is
16 adjusted to deliver additional energy to the seed plasma beyond the
17 threshold level for avalanche breakdown. Gas behind the plasma at 30a is
18 cut off from the laser source, while the newly formed plasma layer at 30b
19 can absorb most of the incident laser energy. This absorbed energy is
20 converted to an ionization shock wave, ionizing successive layers of gas,
21 which in turn optically absorb. The process cascades and the ionization
22 shock wave builds, propagating back toward the laser source. The minor
23 laser absorption wave shown at 30a propagates away from the laser 12
24 and produces diamond particles on the substrate 32. It can be seen in
25 Figure 1 that the substrate 32 is in the optical path of the laser pulse 14.
26 Depending on the energy level of the laser the surface of the substrate 32
27 will be evaporated forming a gas supplementing the absorption wave. The
28 evaporated material from the substrate 32 recondenses and is coated by
29 the material generated by the laser absorption wave 30a forming a
30 diamond film on the substrate 32 or substrates in close proximity such as
31 34. At mid levels of laser energy the substrate of the layer creates a
32 spray of liquid or heated material that act as nucleation centers for
33 accumulating materials generated in the laser absorption wave. At lower
34 energy levels the surface of the substrate 32 is liquefied and the materials
35 created in the absorption wave are welded to the surface of the substrate

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1 32. These particles create a diamond film that resulted from the
2 breakdown of the hydrocarbon gas and hydrogen mixture.

3 There is shown in FIGURE 1a an alternate method of coating a
4 substrate with a diamond film using the laser absorption wave technique.
5 In this embodiment the substrate 32 is reflective. The laser pulses 14
6 from the laser are focused on the substrate such that reflective pulses 36
7 initiate the laser absorption wave 30. In this configuration, energy from
8 the laser pulses 14 are used partially to preheat the substrate 32 and the
9 laser absorption wave is created with the balance of the energy such that
10 the major portion of the wave 30b is now propagating toward the
11 substrate 32. This enhances the diamond deposition rate on the substrate.

12 Referring to FIGURE 2 there is shown a further embodiment
13 incorporating the principles of using a laser absorption wave to deposit
14 diamond on substrates. In this configuration, a substrate 38 is inserted
15 between the laser and the laser absorption wave 30. The substrate 38 is
16 transmissive such that once the laser absorption wave is initiated the
17 major portion of the laser absorption wave 30b travels in the direction of
18 the substrate 38 and coats the substrate 38. It should be appreciated in all
19 of the embodiments shown that both composition and phase of the deposit
20 on the substrate may be changed by variation of the process parameters
21 such as the focal standoff, the distance between the focal point of the laser
22 and the substrate; the laser pulse energy; the laser pulse repetition rate;
23 and the flow rates of the gases. The following table lists examples of
24 process parameters for various substrates:

25

26 Substrate	27 <u>z (mm)</u>	<u>EL(mJ)</u>	<u>fH2</u>	<u>fCH4</u>	<u>T_s</u>	<u>cell</u>
28 tungsten carbide	-12	100	15	0.04	800°	Open
29 440C steel	0	300	15	0.04	800°	Open
30 440C steel	+22	75	30	0.04	30°	Closed
31 graphite (POCO)	0	100	27	0.04	30°	Closed
32 aluminum	+15	300	17	0.20	30°	Closed
33 (2024)						
34 titanium	+20	75	12	0.04	30°	Closed
35 (Ti-6-AR-AV)						
36 silicon	-10	150	12	0.04	30°	Closed

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1 In the table above z = the standoff distance in millimeters where positive
2 standoff is shown in figure 1 and negative standoff is shown in figure 2; EL = th
3 laser pulse energy in millijoules; fH_2 = flow rate of hydrogen in liters per
4 minute; fCH_4 = flow rate of methane in liters per minute; T_s = bulk substrate
5 temperature in degrees centigrade; and cell indicates whether the process was
6 conducted in open air with flame or closed chamber without flame. The proces:
7 was performed with a YAG laser, Q-switched at 1.06 μm , 10 nsec spike, with a
8 repetition rate = 20 Hz. The lens was a f4 focusing lens with a 6" focal length.

9 FIGURE 3 illustrates a further embodiment where the pulses 14 of
10 the laser 12 are focused by the lens 16 onto the target 32 such that the
11 area of substrate liquifies or evaporates to produce an atomized spray or
12 liquid or a solid seed 40. Under conditions where temperature of the
13 individual nuclei is approximately 800-1200°C, the spray 40 is injected
14 into the laser absorption wave which is simultaneously created. When the
15 target 32 is graphite or a high carbon content material, the spray 40
16 provides carbon seeds which are coated by the laser absorption wave 30. in
17 a homogeneous nucleation scheme to produce diamond. Material
18 consolidation forms a film on the substrate 32. Further, material arriving
19 within the optical path 42 and consolidating on the transmissive substrate
20 38 may be used to create an optical coating. Spray nuclei with sufficient
21 momentum to traverse the laser absorption wave 30 through the optical
22 path 42 can create separate particles for use as grit or polishing powder
23 which may be collected on substrate 44.

24 If the substrate material 32 is a metal, the spray 40 then provides
25 solid or liquid metal nuclei that seed the laser absorption wave 30. In this
26 instance the metal condensates are coated with the diamond. The resulting
27 coated particles may then reconsolidate on a substrate such as 32 to
28 produce a metal diamond composite coating. Such a process is facilitated if
29 the metal is still liquid and hence mobile. Metal nuclei escaping through
30 the laser absorption wave 30 may be coated with diamond to create
31 distinct particles of diamond coated metal. Should such conglomerate
32 particles cool before capture on a substrate 44, perfectly spherical abrasive
33 or bearing particles may be formed. If arriving particles still possess
34 liquid cores, the molten metal serves to weld a diamond metal composite
35 to the substrate 44.

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1 FIGURE 3a teaches an alternate embodiment where the laser pulses
2 14 are focused directly on the substrate 32 creating the spray 40. - The
3 precursive gases of hydrogen and hydrocarbon mix are also supplied at
4 this focal point by the nozzle 18 such that the laser absorption wave now is
5 created at the surface of the substrate. This further enhances seeding of
6 the laser absorption wave 30 for developing the diamond like film.

7 FIGURE 4 illustrates an alternate embodiment wherein the laser
8 absorption wave apparatus 10 is modified to incorporate a pulse splitter
9 46 that divides the laser wavefront along a separate optical path 48 such
10 that is it focused by lens 50 upon the substrate 32 so as to preheat it. This
11 configuration wherein part of the laser output pulse is split off to preheat
12 the substrate can be utilized in all of the embodiments hereinabove shown
13 and described.

14 This process can be used to deposit other films such as SiO_2 with O_2
15 as the gas and Si as the sacrificial substrate; Si_3N_4 with N_2 as the gas and
16 Si as the sacrificial substrate; amorphous carbon with carbon vapor as the
17 gas and graphite as the sacrificial substrate; and cubic boron nitride and
18 hexagonal boron nitride with N_2 as the gas and hexagonal boron nitride as
19 the sacrificial substrate.

20 Although there has been illustrated and described a specific
21 structure, it is clearly understood that the same were merely for purposes
22 of illustration and that changes and modifications may be readily made
23 therein by those skilled in the art without departing from the spirit and
24 scope of this invention.

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1 I claim:

2

3 1. A method of coating materials comprising the steps of:

4 a) Providing a source of gas mixture;

5 b) igniting the gas mixture into a flame;

6 c) irradiating the ignited gas mixture with a laser pulse at the
7 threshold avalanche breakdown level of the mixture creating a seed
8 plasma within the mixture;

9 d) adjusting the laser such that the laser has an energy level at a
10 level above the breakdown level creating a laser absorption wave creating
11 precursor fragments of the gas mixture; and

12 e) placing a substrate within close proximity of the laser
13 absorption wave such that the laser absorption wave carries precursor
14 fragments to the substrate wherein the substrate develops a coating
15 comprised of the precursor fragments of the gas mixture.

16

17 2. A method of coating materials as recited in claim 1 further
18 comprising the step of focusing the laser at a point into the mixture at a
19 standoff distance which is the distance between the focal point and the
20 substrate to create the seed plasma.

21

22 3. A method of coating materials comprising the steps of:

23 a) providing a source of gas mixture;

24 b) igniting the gas mixture into a flame;

25 c) irradiating the ignited gas mixture with a laser pulse above the
26 threshold breakdown level of the mixture creating a seed plasma within
27 the mixture that results in a laser absorption wave in the mixture; and

28 d) placing a substrate in the optical path of the laser pulses
29 causing a portion of the substrate to liquefy or evaporate producing a
30 spray or seed plasma of precursor fragments from the substrate that mixes
31 with precursor fragments of the gas mixture in the laser absorption wave
32 wherein the substrate develops a coating comprised of the mixed
33 precursor fragments from the gas mixture and the substrate.

34

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- 1 4. A method of coating materials as recited in claim 1 comprising the
2 step of providing substrate that is transmissive of the laser pulse and
3 placing the substrate between the laser and the source of gas mixture.
4
- 5 5. A method of coating materials as recited in claim 1 wherein the gas
6 mixture is comprised of hydrogen and hydrocarbon compounds and the
7 coating is comprised of diamond.
8
- 9 6. A method of coating materials as recited in claim 3 wherein the gas
10 mixture is comprised of hydrogen and hydrocarbon compounds and the
11 coating is comprised of diamond.
12
- 13 7 A method of coating materials as recited in claim 3 wherein the
14 substrate is metallic.
15
- 16 8. A method of coating materials as recited in claim 8 wherein the gas
17 mixture is comprised of hydrogen and hydrocarbon compounds.
18
- 19 9. A method of coating materials as recited in claim 9 wherein metallic
20 nuclei from the substrate are coated with diamond forming diamond
21 microspheres.
22
- 23 10. A method of coating materials as recited in claim 1 wherein the gas
24 mixture is comprised of O₂, the substrate is comprised of Si, and the
25 coating is comprised of SiO₂.
26
- 27 11. A method of coating materials as recited in claim 3 wherein the gas
28 mixture is comprised of O₂, the substrate is comprised of Si, and the
29 coating is comprised of SiO₂.
30
- 31 12. A method of coating materials as recited in claim 1 wherein the gas
32 mixture is comprised of N₂, the substrate is comprised of Si, and the
33 coating is comprised of Si₃N₄.
34

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- 1 13. A method of coating materials as recited in claim 3 wherein the gas
2 mixture is comprised of N₂, the substrate is comprised of Si, and the
3 coating is comprised of Si₃N₄.
4
- 5 14. A method of coating materials as recited in claim 1 wherein the gas
6 mixture is comprised of carbon vapor, the substrate is comprised of
7 graphite, and the coating is comprised of amorphous carbon.
8
- 9 15. A method of coating materials as recited in claim 3 wherein the gas
10 mixture is comprised of carbon vapor, the substrate is comprised of
11 graphite, and the coating is comprised of amorphous carbon.
12
- 13 16. A method of coating materials as recited in claim 1 wherein the gas
14 mixture is comprised of N₂, the substrate is comprised of hexagonal boron
15 nitride, and the coating is comprised of cubic boron nitride or hexagonal
16 boron nitride.
17
- 18 17. A method of coating materials as recited in claim 3 wherein the gas
19 mixture is comprised of N₂, the substrate is comprised of hexagonal boron
20 nitride, and the coating is comprised of cubic boron nitride or hexagonal
21 boron nitride.
22
- 23 18. A method of coating materials as recited in claim 1 wherein the laser
24 pulse is divided and a portion of the laser pulse is focused on the substrate
25 to preheat the substrate.
26
- 27 19. A method of coating materials as recited in claim 3 wherein the laser
28 pulse is divided and a portion of the laser pulse is focused on the substrate
29 to preheat the substrate.
30
- 31 20. A method of coating materials comprising the steps of:
32 a) providing a source of gas mixture;
33 b) igniting the gas mixture into a flame;
34 c) irradiating the ignited gas mixture with laser pulses having an
35 energy level at the threshold breakdown level of the mixture creating a
36 seed plasma within the mixture;

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1 d) adjusting the laser such that the laser has an energy level
2 above the breakdown level creating a laser absorption wave creating
3 precursor fragments of the gas mixture; and

4 e) placing a first substrate within close proximity of the laser
5 absorption wave and in the path of the laser pulses causing the first
6 substrate to liquefy or evaporate producing a spray or a second seed
7 plasma of precursor fragments from the substrate that mixes with the
8 precursor fragments of the gas mixture in the laser absorption wave, and

9 f) placing a receiving substrate within close proximity of the first
10 substrate wherein the receiving substrate receives a coating comprised of
11 the mixed precursor fragments from the gas mixture and the first
12 substrate.

13

14 21. A method of coating materials as recited in claim 25 further
15 comprising the step of focusing the laser at a point into the mixture at a
16 standoff which is the distance between the focal point and the first
17 substrate to create the second seed plasma.

18

19 22. A method of coating materials as recited in claim 25 wherein the
20 first substrate is metallic.

21

22 23. A method of coating materials as recited in claim 25 wherein metallic
23 nuclei from the first substrate are coated with diamond, forming diamond
24 microspheres.

25

26 24. A method of coating materials as recited in claim 25 wherein the
27 laser pulse is divided and a portion of the laser pulse is focused on the
28 substrate to preheat the substrate.

29

30 25. A method of coating materials comprising the steps of:

31 a) providing a source of gas mixture;

32 b) igniting the gas mixture into a flame;

33 c) irradiating a reflective substrate with laser pulses having an
34 energy level above the threshold breakdown level of the gas mixture
35 creating a laser absorption wave in the gas mixture after reflection from
36 the substrate and further causing a portion of the substrate to liquefy or

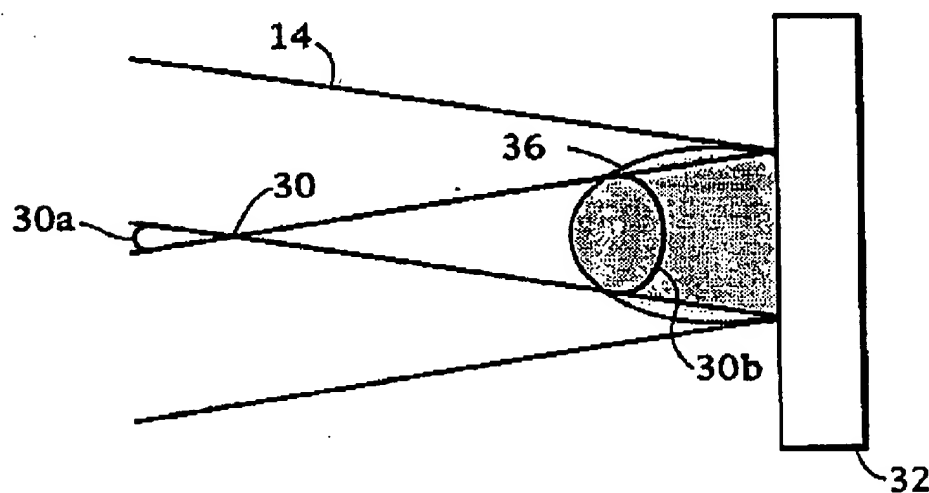
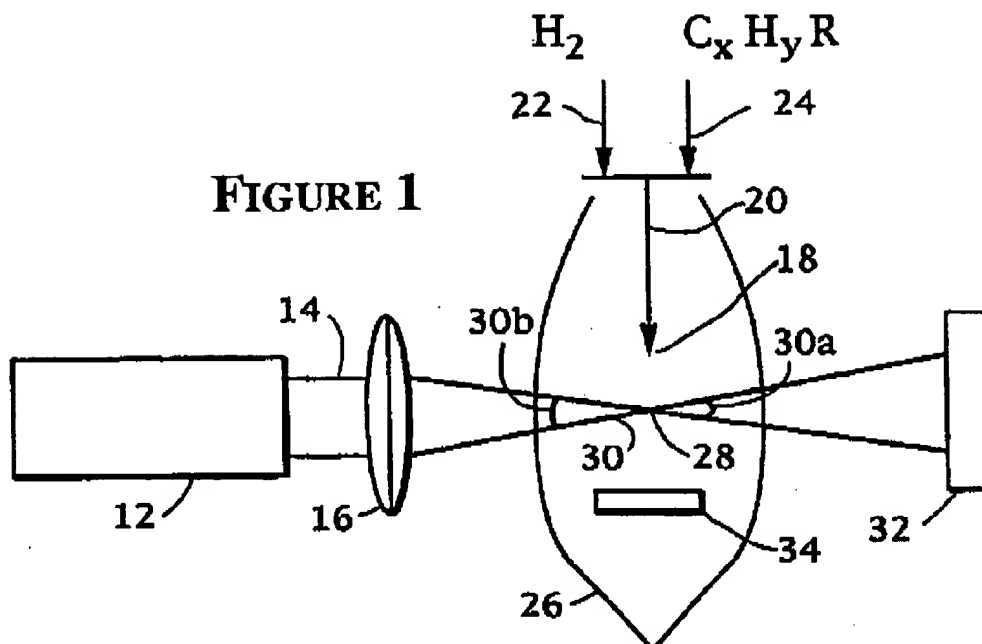
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1 evaporate producing a spray or seed plasma of precursor fragments from
2 the substrate that mixes with precursor fragments of the gas mixture in
3 the laser absorption wave wherein the substrate develops a coating
4 comprised of the mixed precursor fragments from the gas mixture and the
5 substrate.
6
7 26. A method of coating materials comprising the steps of:
8 a) providing a source of gas mixture into a closed chamber;
9 b) irradiating the gas mixture with a laser pulse at the threshold
10 breakdown level of the mixture creating a seed plasma within the mixture;
11 c) adjusting the laser such that the laser has an energy level at a
12 level above the breakdown level creating a laser absorption wave
13 containing precursor fragments of the gas mixture; and
14 d) placing a substrate within close proximity of the laser
15 absorption wave such that the laser absorption wave carries the precursor
16 fragments to the substrate wherein the substrate develops a coating
17 comprised of the precursor fragments of the gas mixture.
18

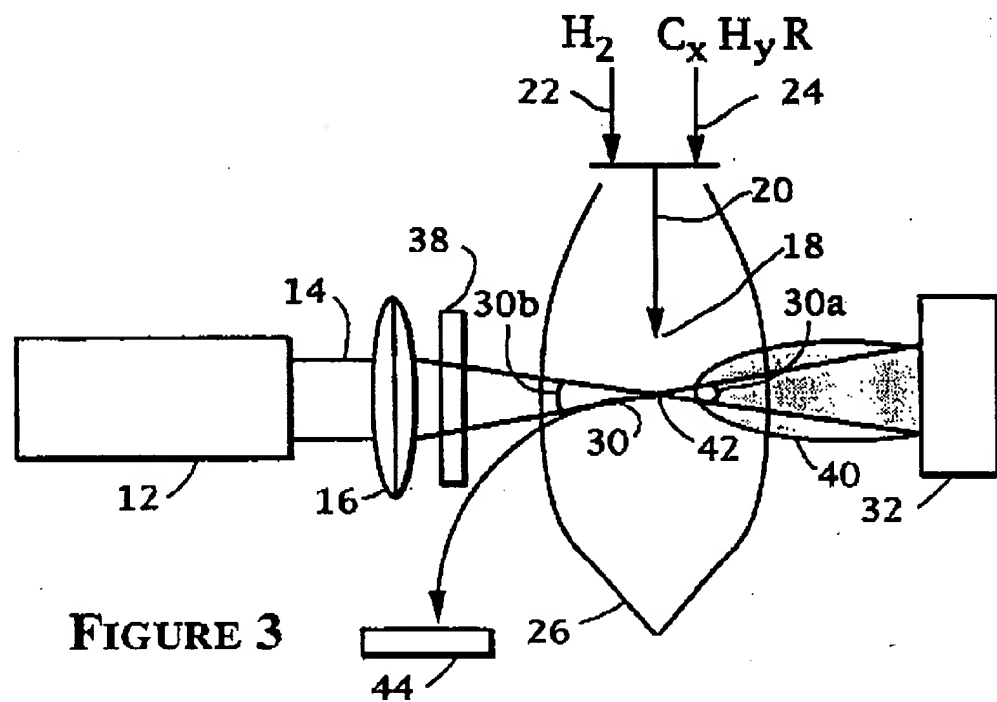
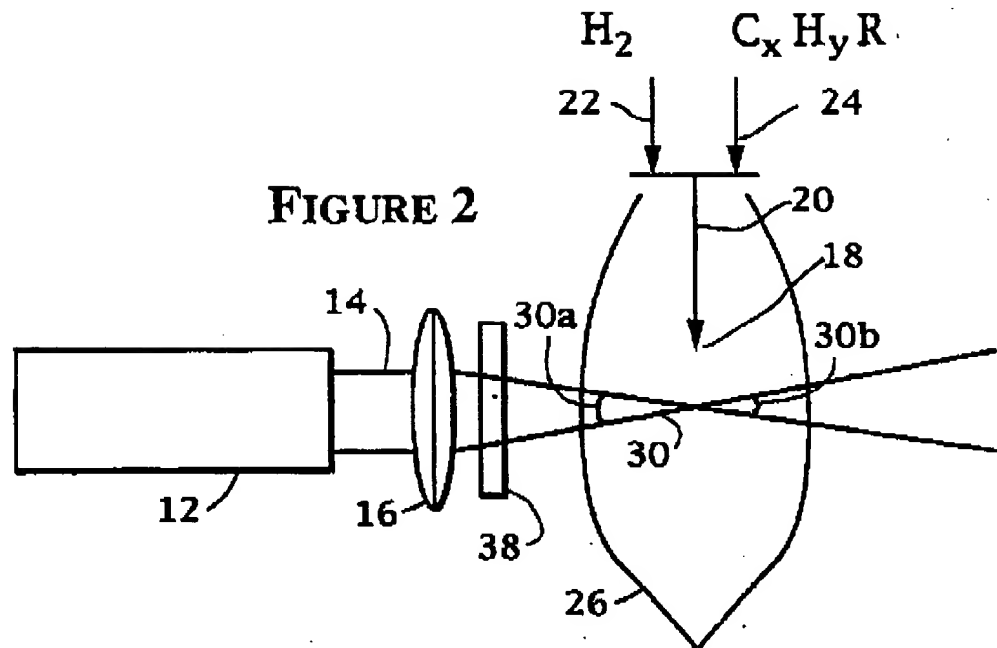
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**FIGURE 1a**1 / 3
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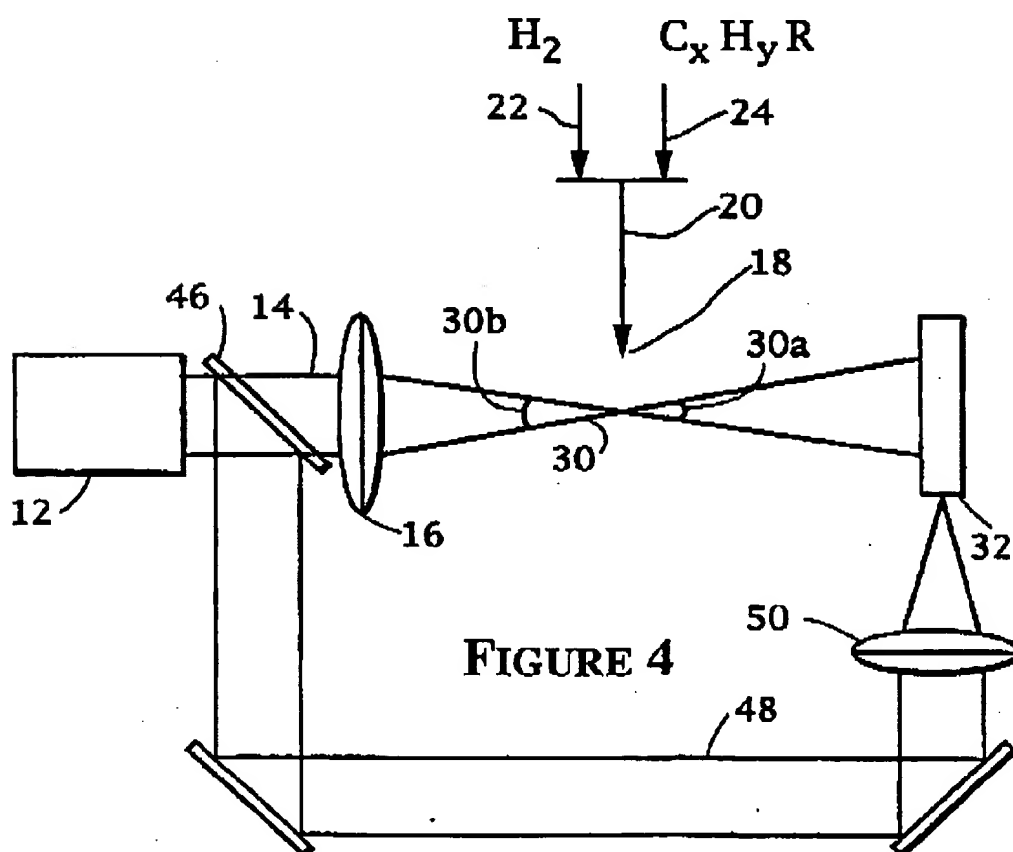
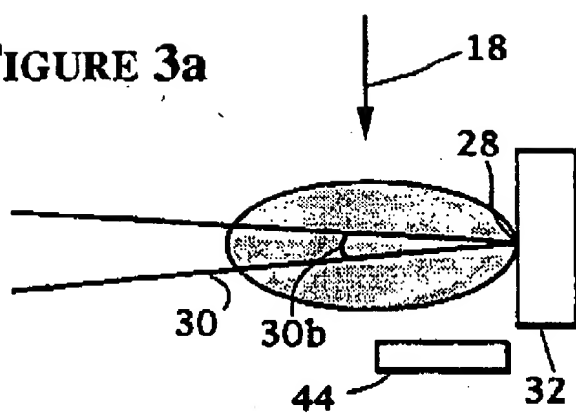


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FIGURE 3a**FIGURE 4**

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INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : B05D 3/06, 7/00

US CL : 427/561,582,583,584,586,596,597,216

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/561,566,582,583,584,586,596,597,554,555,556,216

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	John F. Ready, <u>Effects of High-Power Laser Reduction</u> , Academic Press, N.Y. 1971, p. 219-220.	1-26
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☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*+ later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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